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The Incompatibility of Certain Alcohol and Soap Frothers

John Thomas Doherty

Doherty, J.T.

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A Thesis

Submitted To The Department of Mineral Dressing

In Partial Fulfillment Of The

Requirements For The Degree Of

Bachelor Of Science In Metallurgical Engineering

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Introduction

It has been known for a number of years that certain organic chemicals, when used singly in the flotation circuit function as excellent frothers, yet where mixtures of these substances are used, frothing is diminished or is entirely destroyed. Thus, Coghill and Clemmer (1) reported that "If colloid chemists have tested the frothing properties of mixtures of pine oil and soap, they must have reported that in certain ratios these reagents are incompatible. When a dilute soap solution is shaken in a test tube in the presence of an increasing amount of pine oil, its sudsing proclivities gradually disappear until no froth can be formed by shaking. With an excess of pine oil, a froth again appears." Again, Wark (2) comments as follows: "Among the many unexplained phenomena of flotation is the combined influence of more than one organic compound on frothing. There are few data available concerning mixtures but Foulk has found that two frothers, one of which is positively adsorbed, the other negatively, may prevent one another from producing stable froths. Bartsch and Halbich also found that a second frother may annul the effects of the first. Bartsch suggests that a mutual lowering of solubility may be responsible for the lower frothing power."

Schuhmann (private communication) (3) has recently stated "I think (that frother incompatibility) has been causing me a great deal of trouble in some soap flotation work I have

been doing lately, but this has been practical work with no time allowed for the proper study of really interesting problems."

The purpose of this thesis is to elucidate this phenomena of frother incompatibility, and to offer an explanation based upon several divergent lines of investigation. The research was limited to four common frothing agents, namely, pine oil, n-amyl alcohol, sodium oleate, and sodium lauryl sulphate (Dreft). Of these reagents, the first two are organic alcohols widely used in sulphide flotation, sodium oleate is a common frother and collector used in non-sulphide flotation, and Dreft is a commercially available detergent, not used as far as the author is aware, in flotation.

ACKNOWLEDGEMENT

The writer wishes to express his appreciation to Dr. S.R.B. Cooke for his many helpful suggestions and generous supervision of this work.

Also, special thanks is given to Dr. A.E. Koenig for equipment borrowed from the Chemistry Department and for suggestions concerning their use.

INITIAL INVESTIGATION

Various investigators have expressed difficulty in quantifying "frothing power." Taggart, et.al., (Trans, A. I.M.E.; Milling Methods; 1930; (page 307)) used an experimental pneumatic flotation cell operating under carefully controlled conditions, but which gave results which were only of " semi-quantitative significance". Wark discusses several types of apparatus used for the same purpose. Perhaps the most satisfactory apparatus is that of Alejnikoff (illustrated on page 260 of "Principles of Flotation" by I.W. Wark).

Accordingly, a modification of this last mentioned apparatus was built. As may be seen from the accompanying photograph, the apparatus consisted of a glass cylinder into the bottom of which was sealed a fritted-glass membrane similar to the Jena glass filter. Air, under pressure controlled by a two-way valve, passed through the filter and into the glass column which contained an aqueous solution of the organic frothing reagent or mixture of reagents. This produced a froth column, the height of which was easily measured. A mercury-filled manometer was connected to the air circuit at the two-way valve. By such an arrangement the air pressure could thus be regulated and a constant pressure could be maintained. The glass filter was sealed into the bottom of the cylindrical frothing column with ordinary sealing wax. The apparatus is illustrated in Figure 1.

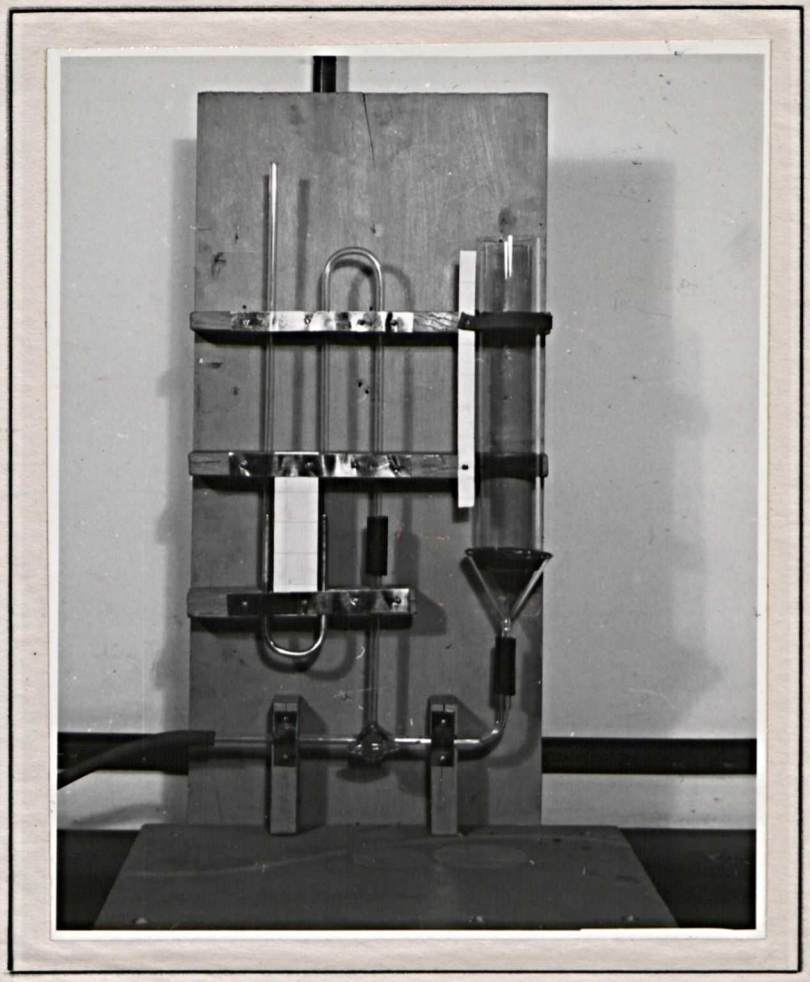


Figure 1

FROTH-MEASURING APPARATUS

A-Frothing Column; B-Fritted-glass Filter; C-Scale
D-Manometer; E-Two-way Valve; F-Scale(Air Pressure)

Because of war conditions, ordinary Jena fritted-glass filters were not obtainable. Similar filters were manufactured in the laboratory by the following technique:

Pyrex glass was ground in a mortar and sized on Tyler screens. Fractions ranging from 28-mesh through 100-mesh were tested. The glass was tamped into a graphite mold of requisite diameter, and placed in a furnace.

In the initial experiments an assay furnace was used for fritting, but the resulting glass shapes were not satisfactory because of lack of controllability of furnace temperature. Later and more successful experiments were conducted in an electric furnace having positive temperature control.

Perfect glass membranes were not made, but reasonably satisfactory results were obtained using minus 65-mesh plus 100-mesh Pyrex and twelve to fifteen minutes exposure to a temperature of 900 degrees Centigrade. The main difficulty with the membranes made by the procedure described was that the pore size was not uniform. Undoubtedly, more carefully controlled fritting conditions would give perfect or nearly perfect membranes.

In an apparatus of this type the porous plate should have uniform pore size. Otherwise, as the air pressure is increased bubbles first form at the larger pores, then with each further increase of pressure smaller and smaller pores come into operation until finally all are gassing freely. Naturally, all of the bubbles produced are not of the same

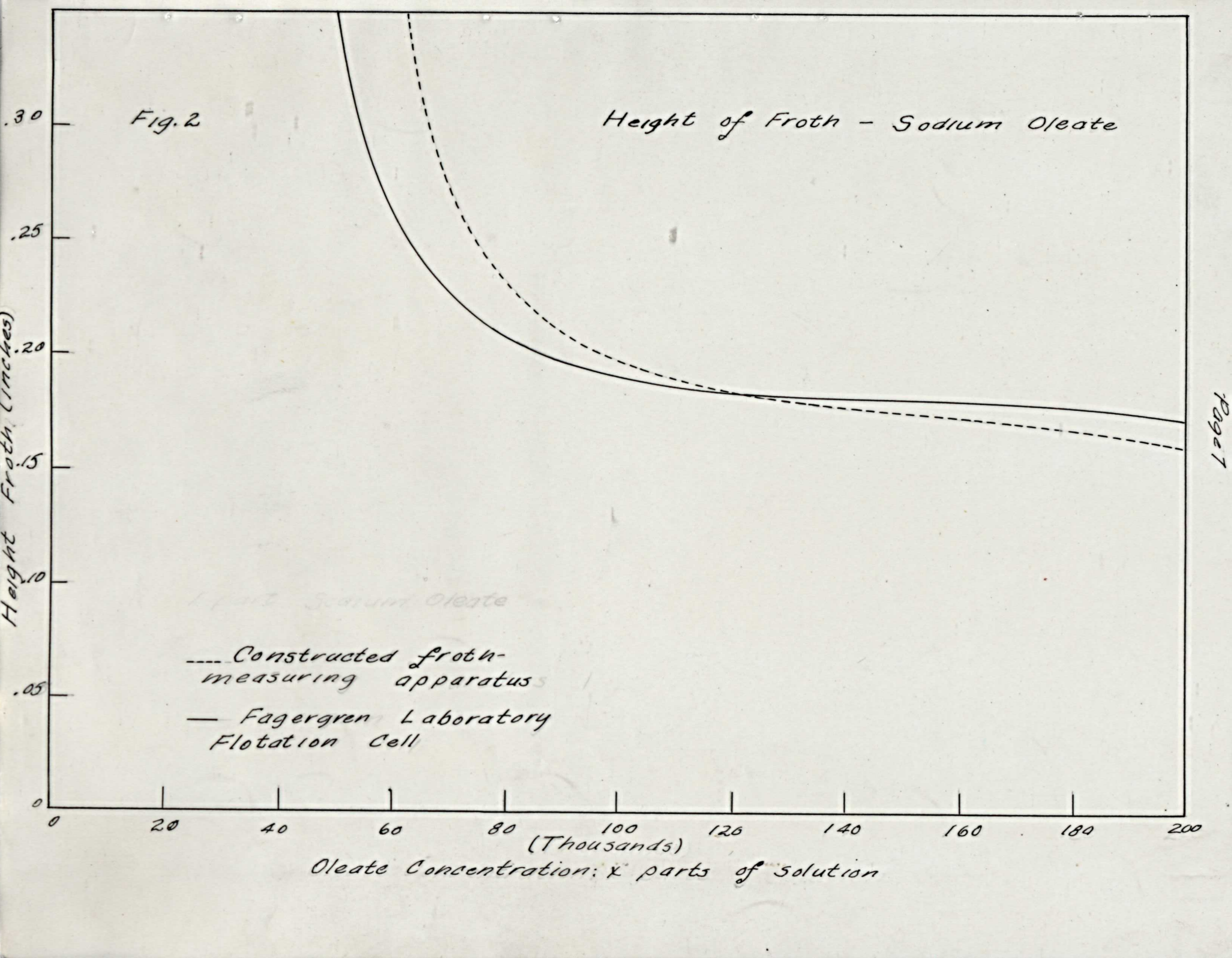


Fig. 2
Height of Froth - Sodium Oleate
Height Froth (inches)
.30
.25
.20
.15
.10
.05
0
0
20
40
60
80
100
120
140
160
180
200
(Thousands)
Oleate Concentration: x parts of solution
---- Constructed froth-measuring apparatus
— Fagergren Laboratory Flotation Cell

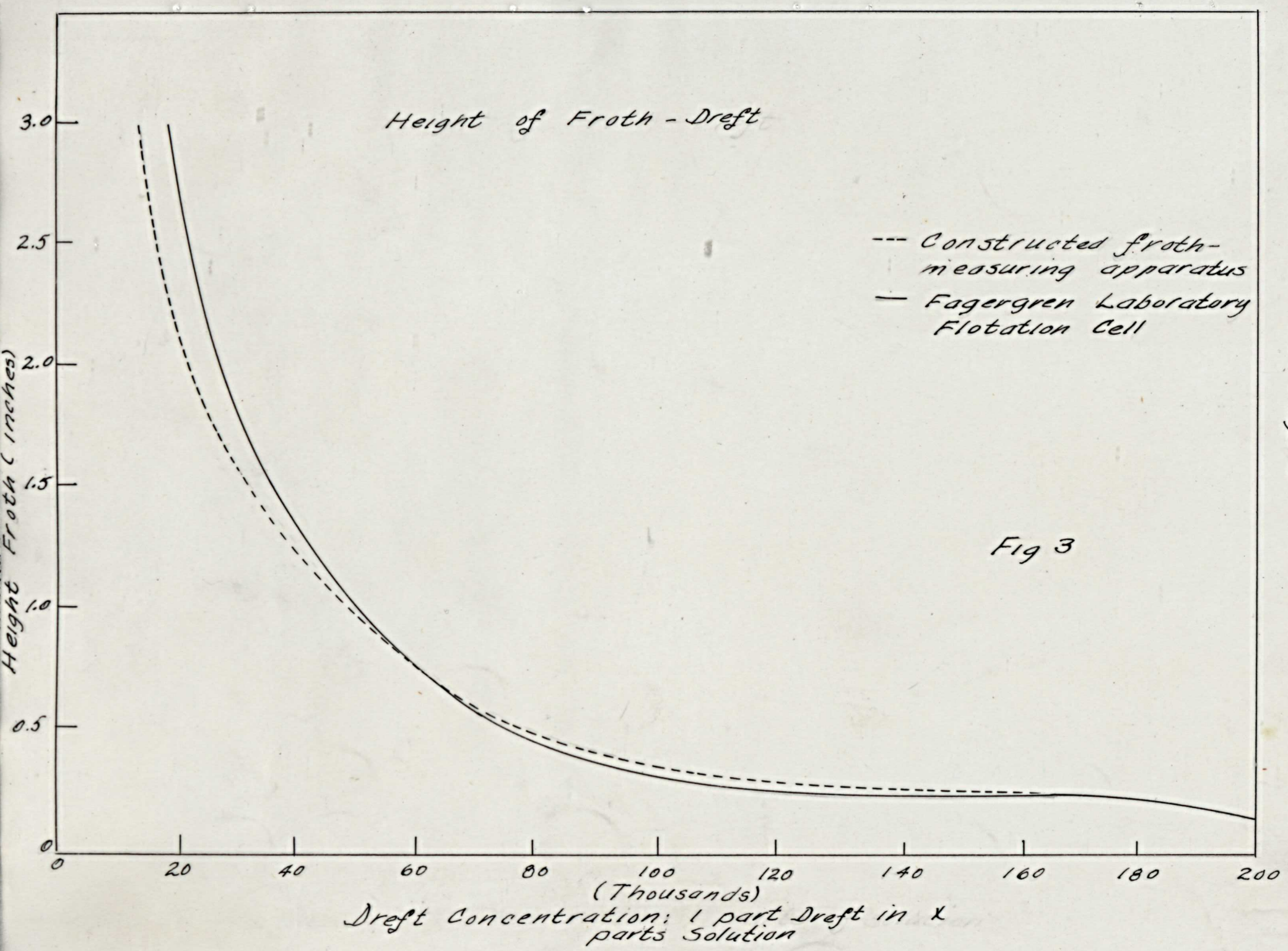

Height of Froth - Dreft
--- Constructed froth-measuring apparatus
— Fagergren Laboratory Flotation Cell
Height Froth (inches)
3.0
2.5
2.0
1.5
1.0
0.5
0
0
20
40
60
80
100
120
140
160
180
200
(Thousands)
Dreft Concentration: 1 part Dreft in X parts Solution

Fig 3

diameter. Rudolf has shown, firstly, that the larger the pore size the larger are the bubbles, and secondly, (confirming an observation of Halberstadt and Prausnitz) (4), that the addition of any frother reduces the size of bubbles, i.e., increases the degree of dispersion. This last effect is to be expected from any substance that lowers the surface tension. (5)

Froth height measurements were first made with separate solutions of Dreft and sodium oleate of concentrations ranging from one part of Dreft in two hundred thousand parts of solution up to one part of Dreft in twenty thousand parts of solution; and one part of sodium oleate in sixty-five thousand parts of solution to one part of sodium oleate in one million parts of solution. Following this runs were made on mixtures of the two reagents each time keeping the concentration of the sodium oleate constant and varying the cumulative amounts of Dreft.

Figures 2 and 3 show results obtained for various concentrations of sodium oleate and Dreft in the frothing apparatus. The results are normal and show decreasing frothing power for successively greater dilution of frother.

Figure 4 shows the gradual destruction of froth, for a constant oleate concentration, with increasing additions of Dreft. This is the phenomenon under investigation.
In order to have a check on the validity of the results obtained by using the pneumatic frothing apparatus, another series of runs was made, this time using the agitation method

of froth formation. To accomplish this a Fagergren Laboratory Flotation Cell (Figure 5) was used. As before, a series of runs was first made on the pure solutions. Later, runs were made on mixtures ranging through the same series of concentrations. The concentration of the variable constituent was cumulatively increased in each case. The results are shown in Figures 2,3,4,6,7, and 8.

In Figure 8, change from one "type" of froth to another at the point of minimum frothing is indicated. Just what the writer means by "type" of froth is difficult to elucidate and impossible to quantify. Thus with pine oil and sodium oleate, less than three cubic centimeters of sodium oleate gave a typical oleate froth.

Further, in Figure 8, a frothing minimum is indicated for pine oil and oleate. A change of pine oil concentration should shift the minimum right or left, depending upon whether the pine oil is decreased or increased. Other tests have shown this statement to be valid.

In tests shown in Figures 4,6, and 7, the oleate concentration was never sufficiently high to destroy the pine oil froth and initiate the oleate froth.

The results of the preceding experiments clearly demonstrate the reality of the phenomenon under investigation. The experiments which follow were conducted to build a basis for the explanation of this phenomenon.

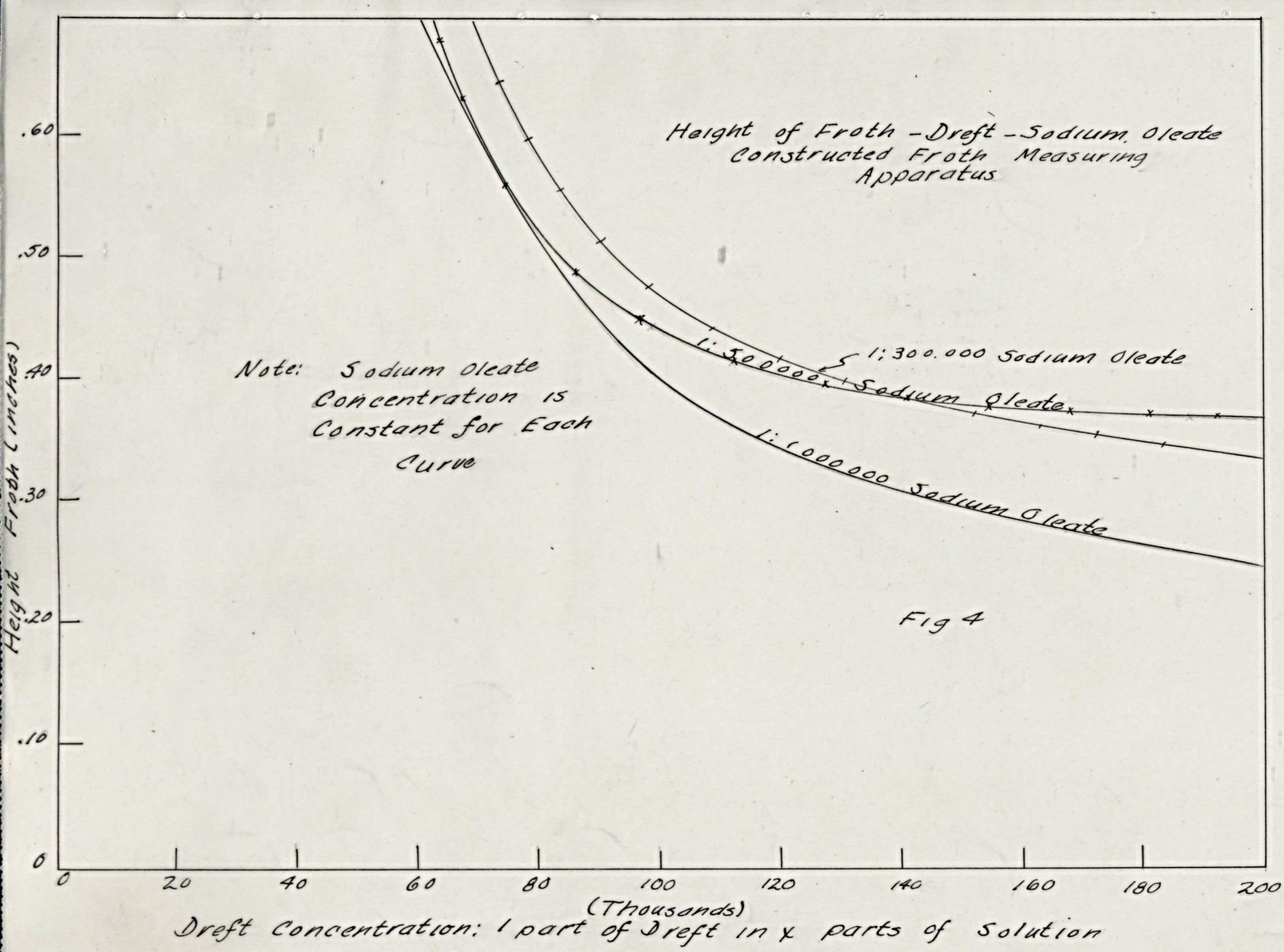

Height of Froth - Dreft - Sodium Oleate
Constructed Froth Measuring
Apparatus
Note: Sodium Oleate
Concentration is
Constant for Each
Curve
1:300.000 Sodium Oleate
1:300'000 Sodium Oleate
1:1000000 Sodium Oleate
Height Froth (Inches)
.60
.50
.40
.30
.20
.10
0
0
20
40
60
80
100
120
140
160
180
200
(Thousands)
Dreft Concentration: 1 part of Dreft in x parts of Solution

Fig 4

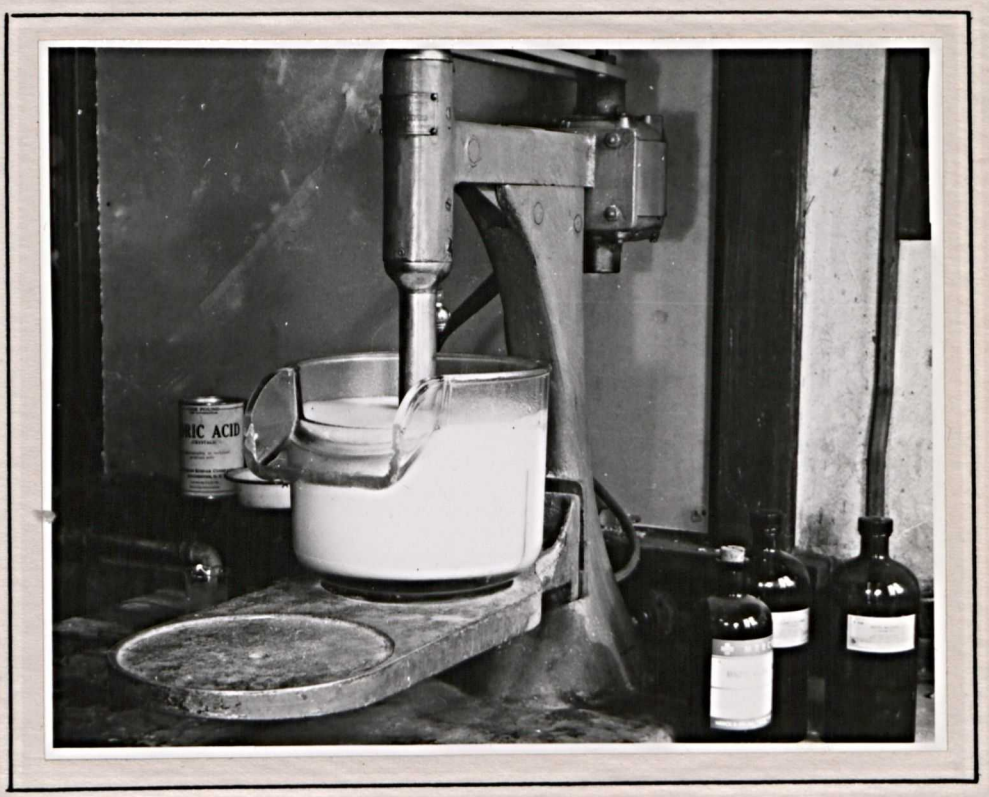
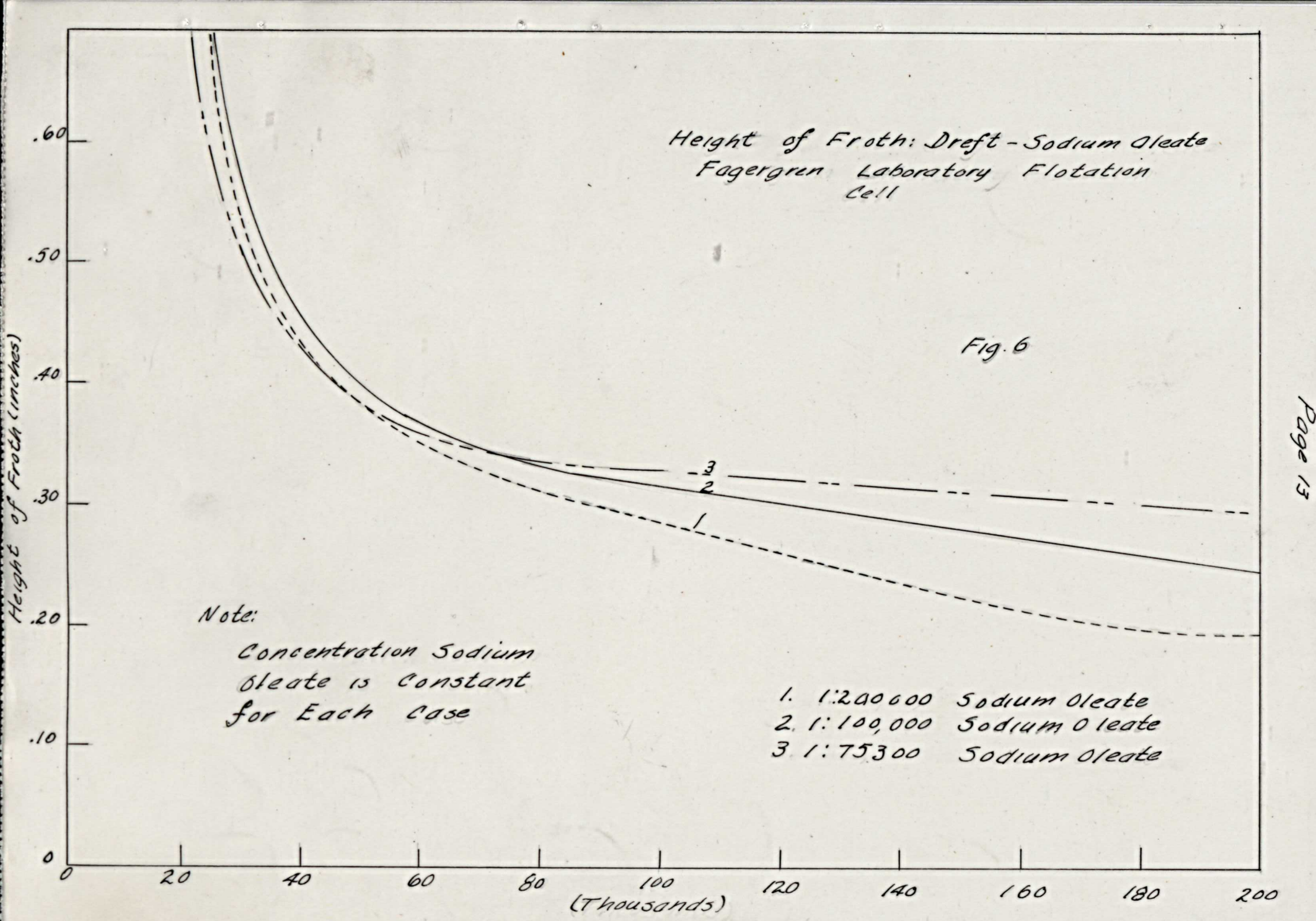
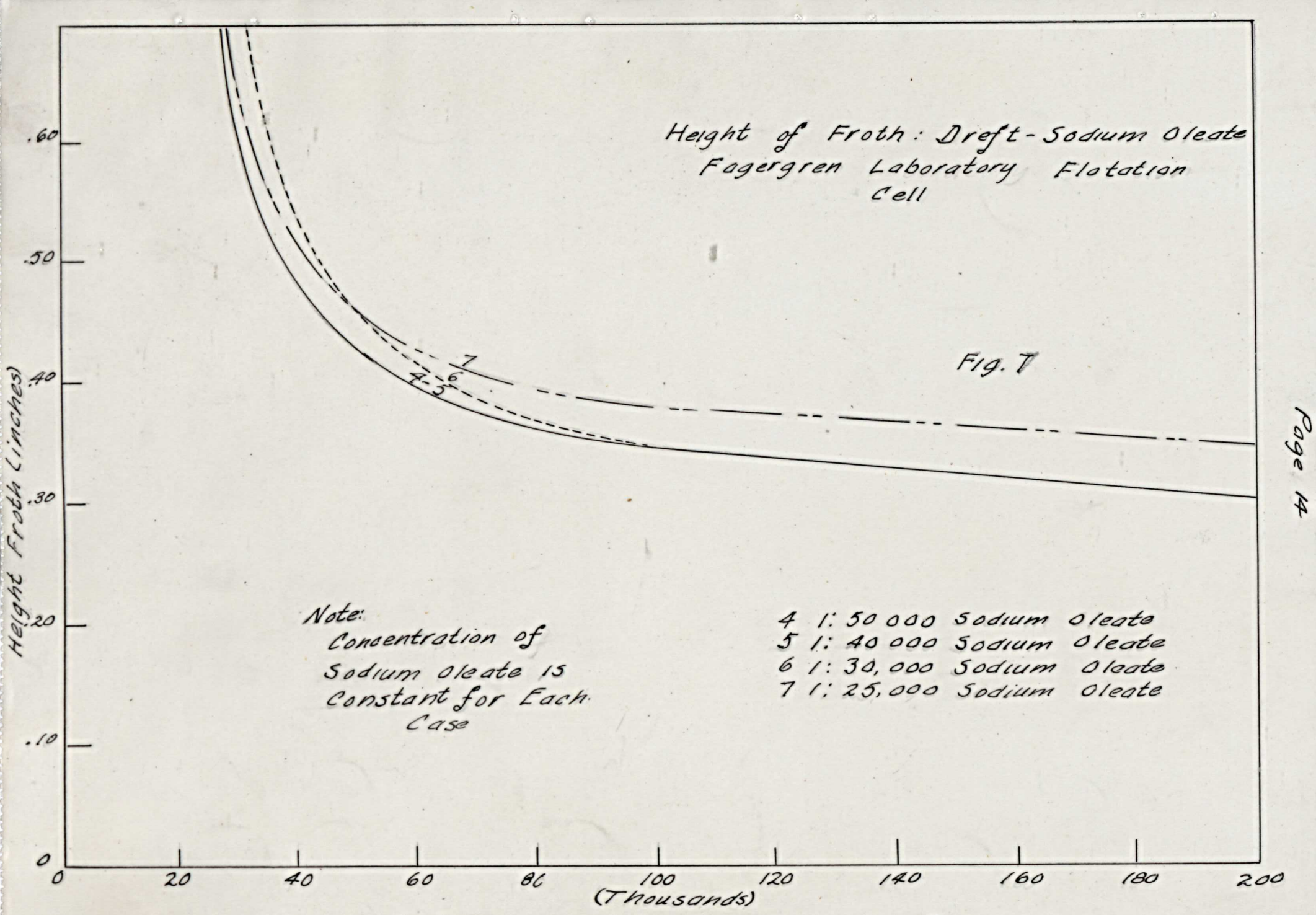


Figure 5

Fagergren Laboratory Flotation Cell


Height of Froth: Dreft - Sodium Oleate
Fagergren Laboratory Flotation Cell
Fig. 6
Height of Froth (inches)
.60
.50
.40
.30
.20
.10
0
0
20
40
60
80
100
120
140
160
180
200
(Thousands)
3
2
1
Note:
Concentration Sodium Oleate is Constant for Each Case
1. 1:200600 Sodium Oleate
2. 1:100,000 Sodium Oleate
3 1:75300 Sodium Oleate
Dreft Concentration: 1 part of Dreft in x parts of Solution


Height of Froth: Dreft-Sodium Oleate
Fagergren Laboratory Flotation Cell
Fig. 7
Note:
Concentration of Sodium Oleate is Constant for Each Case
4 1: 50 000 Sodium Oleate
5 1: 40 000 Sodium Oleate
6 1: 30,000 Sodium Oleate
7 1: 25,000 Sodium Oleate
Height Froth (inches)
.60
.50
.40
.30
.20
.10
0
0
20
40
60
80
100
120
140
160
180
200
(Thousands)
Dreft concentration: 1 part Dreft in x parts of Solution

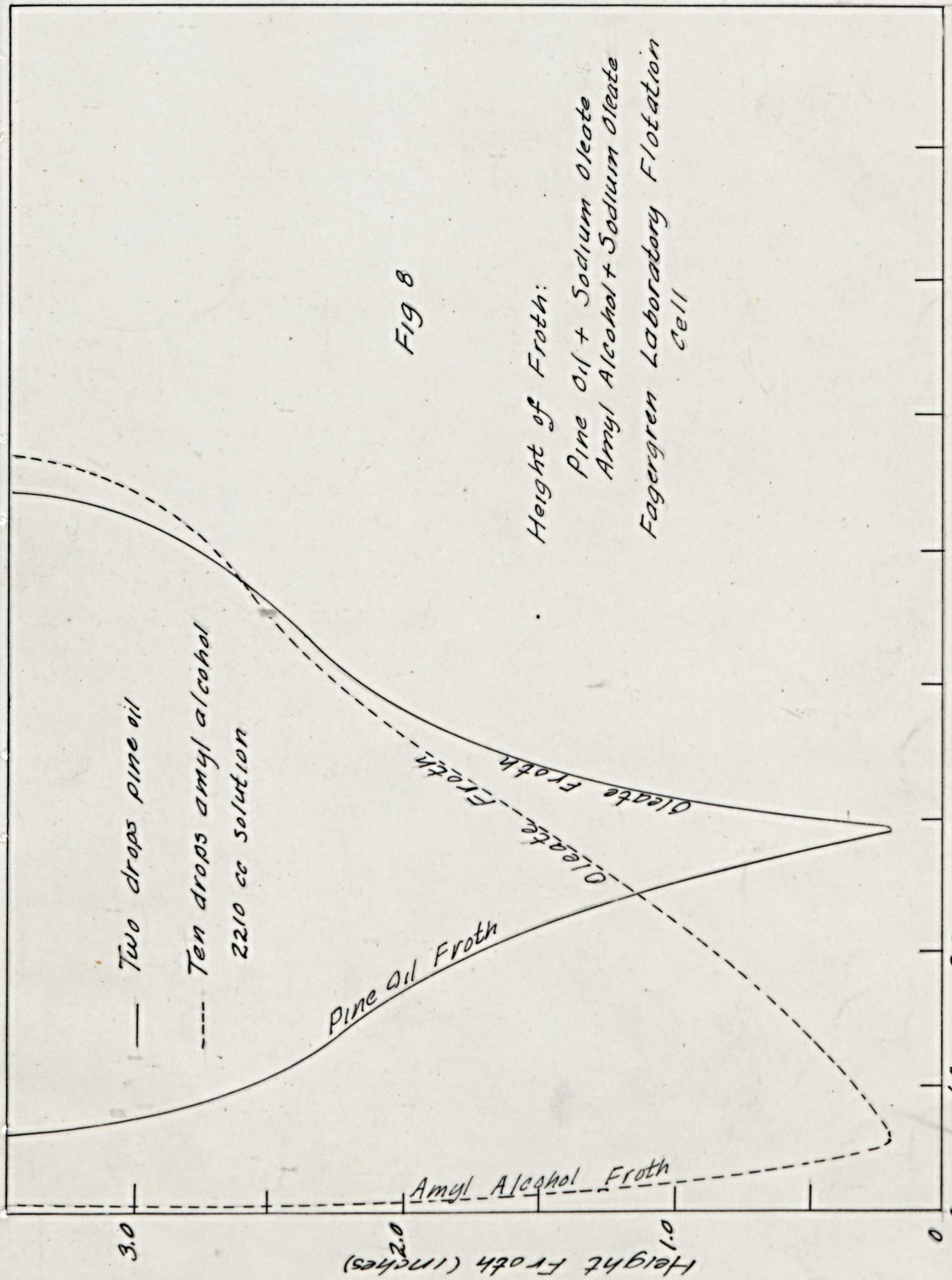


Fig 8
Height of Froth:
Pine Oil + Sodium Oleate
Amyl Alcohol + Sodium Oleate
Fagergren Laboratory Flotation Cell
— Two drops pine oil
--- Ten drops amyl alcohol 2210 cc solution
Oleate Froth
Oleate Froth
Pine Oil Froth
Amyl Alcohol Froth
Height Froth (inches)
3.0
2.0
1.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
1% Sodium Oleate Solution (cc)

FROTHING AND SURFACE TENSION

Pure liquids do not froth, i.e., if they are placed in a test tube and agitated by introducing air, or by violently shaking, no froth will be formed. Liquids consisting of two or more constituents which in the pure state differ widely in surface tension and are in mutual solution can be made to froth.

Frothing is nil, both for pure water and for saturated solutions. Maximum frothing is obtained at approximately that concentration at which the surface tension-concentration curve is most distant from the straight line connecting the surface tensions of pure solvent and of saturated solutions.

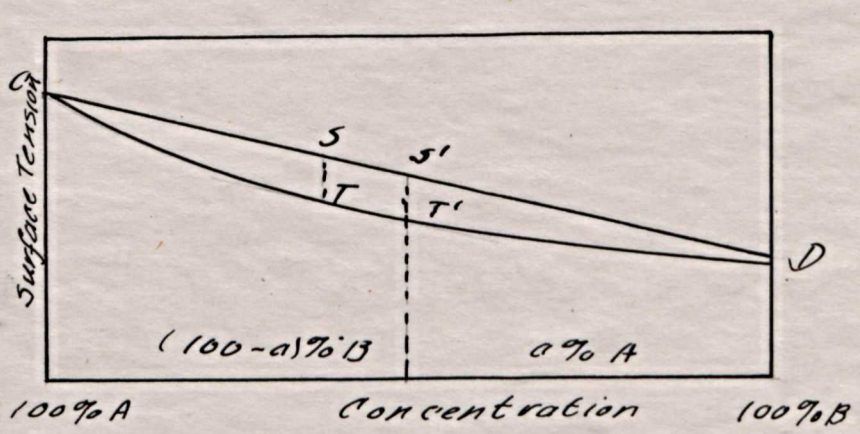
A small amount of dissolved substance may decrease the surface tension of the solvent considerably, but may increase it only slightly.

Szyskowski's data (Bohdan von Szyskowski, Zeit. Physik. Chem. (1908) 64 385-414) show that in the case of very dilute solutions the concentration of the solute, and the surface tension, are related by a straight-line law, in the case of concentrated solutions by a logarithmic law, while with intermediate concentrations the relation between the two is variable.

According to Taggart and Gaudin (6): "The efficacy of dissolved substances in stabilizing froths does not lie in lowering surface tension of the solution, but in imparting to the surface tension the properties of variability and adjustment to imposed strains.

"The soluble substance changes the surface tension considerably more than it would if no adsorption took place. Agitation results in bringing to the surface portions of the liquid that were in the bulk thus forming new surfaces with higher tension than that of the old air-liquid surfaces and having, therefore, a tendency to diminish toward an equilibrium value which is that of static surface tension. If a film, after reaching a static surface tension, is stretched, it thins down and liquid from the inner part reaches the surface. This liquid, because of its lesser concentration in the solute will have a higher surface tension than that of the old film and, hence, will counteract the force that tends to break the film. Thus, the presence of a soluble substance in solution causes bubble films to have an adjustable surface tension and between the limits of the surface tension of the adsorbed film and that of the bulk of the liquid, to act as a film of rubber. Maximum range of adjustability will correspond to maximum frothing power."

"Let the accompanying figure represent an ideal case: (6)



"eSS'D is a hypothetical concentration-surface tension curve for the bulk of the liquid, which cannot be confirmed by experiment. It assumes a straight line relation, as any other assumption would be unjustified. CTT'D is the corresponding curve for the surface film from experiment. The distance S'T between the two curves is the measure of the frothing power of the mixture containing a percent of solvent A, and (100 - a) percent of solute B. Point T, at which the tangent to the curve CTT'D is parallel to CSS'D, corresponds to the greatest frothing power.

Generally, frothing is greatest for solutions having a concentration about one-half the saturation concentration decreasing to zero for pure water and to a comparitively small figure for saturated solutions. The distance between the hypothetical bulk surface tension curve and the actual surface tension curves for sodium oleate and Dreft is a maximum in the neighborhood of this same concentration."

Tests show that saturation marks a critical point in the frothing of solution and that beyond the saturation point the mixture behaves much like a pure liquid or a mixture of two liquids mutually insoluble. This is explained on the supposition that the range in surface tension between the static and dynamic surface tensions is so small in the case of saturated solutions that too little variability in surface tension of films is available for adjustment to strains induced in the bubble-making operation.

Thomas (7) states that, "Frothing agents' molecules must pass readily into the interface between water and air and in order to do this they must lower the air-water surface tension markedly when present in the surface in small quantities. The properties that a molecule must possess in order to pass into a spread readily at an air-water interface are water repulsion and water avidity. Without water repulsion there is no tendency for a molecule to pass from water into air nor opposition to its return into the water if it comes to the water surface. With water avidity molecules that reach the water surface aggregate there and do not spread out and any effect they have is localized. Since these two necessary properties are exactly opposite, if they are to have any useful effect and not merely neutralize each other, they must not be properties of the molecule as a whole, but of parts and of different parts of the molecule, that is, one part of the molecule must be water-repellent and one part water-avid. Furthermore, the water-repellent part which will be the part in contact with the air, must be of a composition such that its surface tension will be markedly different from that of water and this specification carries in its train the further requirement that it be lower than water. The common and characteristic compounds of low surface tension are the hydrocarbons which are characteristically water repellent. The characteristic water-avid groups are OH, COOH, CO, NH_2, NO_2, NO, and COC, ordinarily oxygen-bearing groups. Thus, a hydrocarbon group combined with one of the above would be expectedly a frothing agent."

" Also, an important phenomena is adsorption which is a process of rearrangement of a system, which results in establishing a difference in concentration, as between the interfacial layers and the bulk of the phases. Rearrangement occurs in such a way that the energy of the interface is reduced by concentration of the dispersed substance. The diminished energy is shown by a decrease in surface tension. For adsorption to occur in a two-phase system, it is necessary that one of the phases at least be of such nature that segregation can take place in it. In a two-phase system composed of pure substances, no adsorption can take place; in a system composed of air and a solution of hydrocarbon in water adsorption can and will take place."

Surface Tension Measurements

Since surface energies are of such significance in froth formation, the writer attempted to follow by surface tension measurements the previously reported changes in frothing obtained by mixing reagents. Special attention was given to pine oil-sodium oleate solution mixtures, and to n-amyl alcohol-sodium oleate solution mixtures.

Surface tension measurements were made on a du Nouy tensiometer (Figure 9). Extreme care was exercised in cleaning glass containers, beakers, the platinum ring, and in using doubly distilled water for all the reagent solutions. Solutions were brought to constant temperature in a thermostat before measuring surface tensions. Determinations were repeated on each solution until a constant reading was obtained.

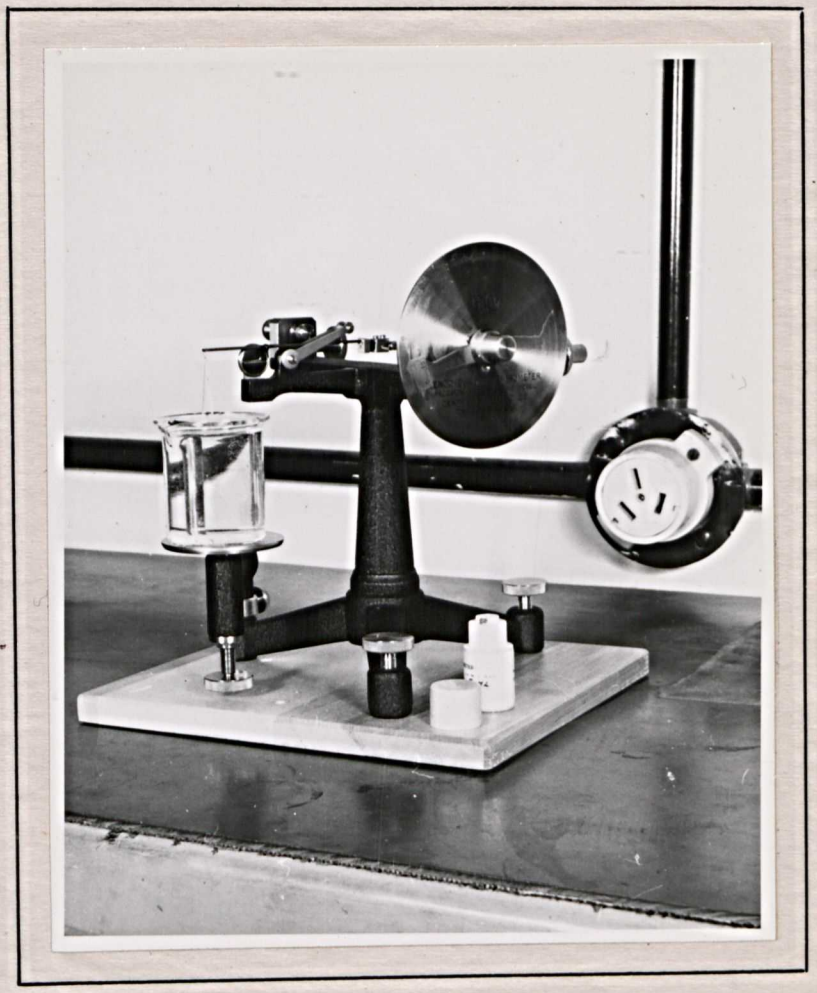


Figure 9

Du Nouy Tensiometer

The ring method gave reproducible results, and further, the results with sodium oleate agreed precisely with those obtained by de Witt and co-workers (8). In accord with the statement on page 18, maximum frothing occurred at a concentration of solute giving maximum difference between the actual surface tension curve and the bulk surface tension curve, Figure 10.

Figure 11 shows the changes in surface tension obtained by adding increasing amounts of sodium oleate to a constant concentration of pine oil in water. The curve should be compared with that for sodium oleate alone given in Figure 10.

It is obvious that there is no marked change from the sodium oleate curve and it is questionable if those changes shown are subject to analysis. The results presented in Figure 11 were also obtained on a second run under identical conditions, so that reality of the curve is established.

Gibb's Adsorption Theorem is stated as follows:

$$U = \frac{C}{RT} \frac{dT}{dC}$$

where,

U is the adsorption in gram molecules per square centimeter of surface.

C is the bulk concentration in gram molecules per liter.

R is the gas constant which is 8.32×10^7 ergs per degree Centigrade.

T is the Absolute temperature

dT/dC is the slope of the surface tension curve.

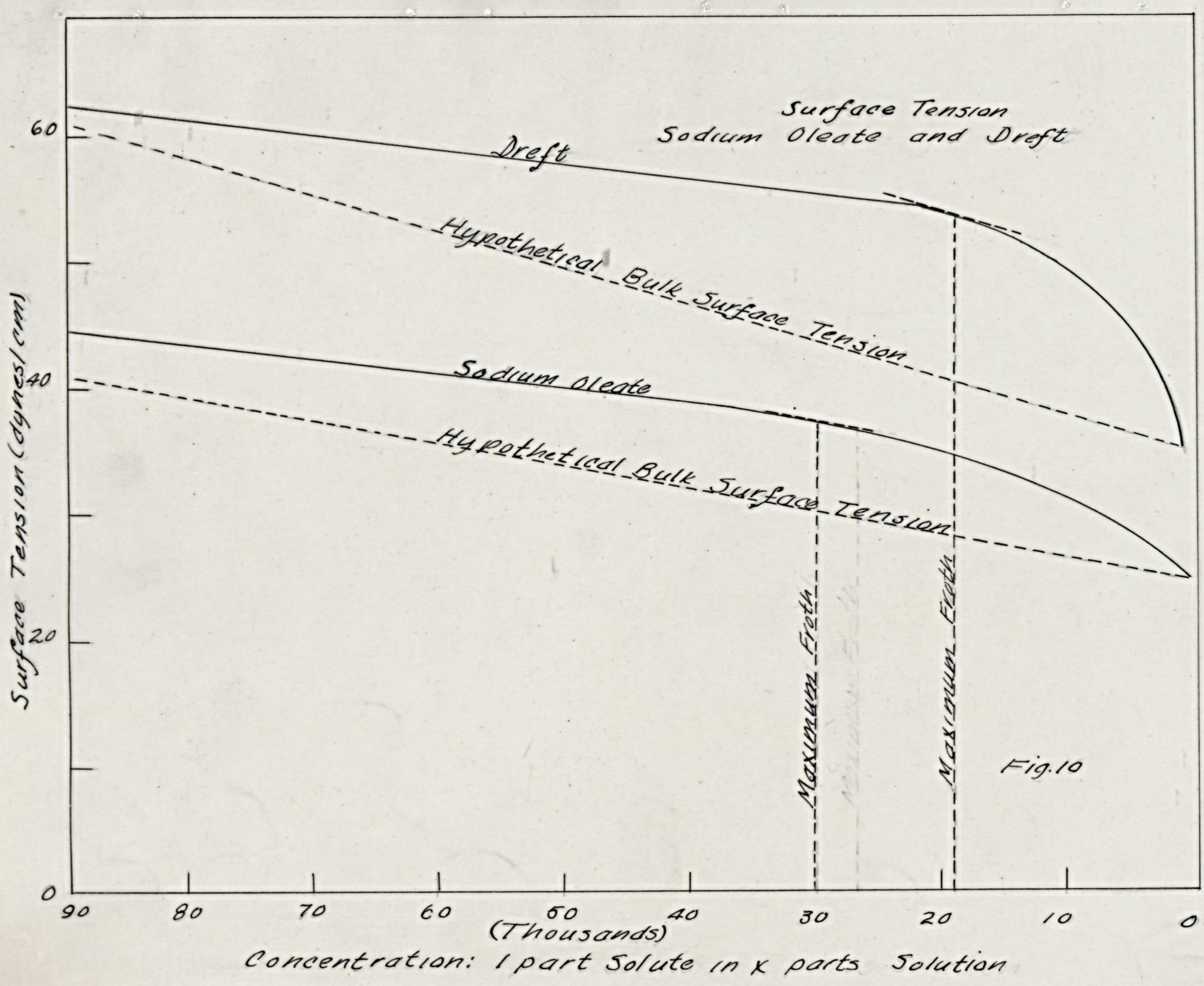

Surface Tension
Sodium Oleate and Dreft
Dreft
Hypothetical Bulk Surface Tension
Sodium Oleate
Hypothetical Bulk Surface Tension
Maximum Froth
Maximum Froth
Surface Tension (dynes/cm)
60
40
20
0
90
80
70
60
50
40
30
20
10
0
(Thousands)
Concentration: 1 part Solute in x parts Solution

Fig. 10

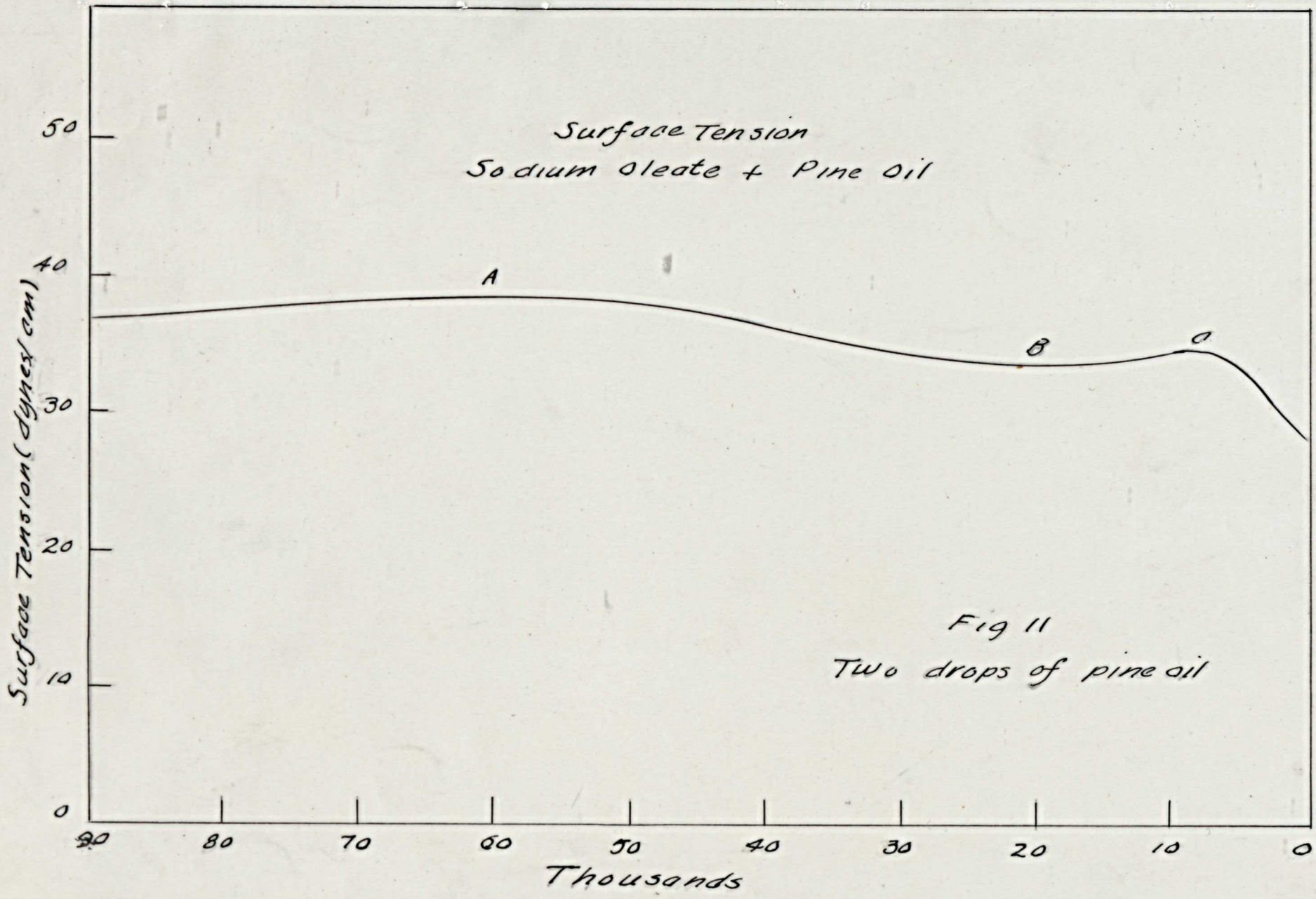


Fig 11
Two drops of pine oil

The validity of this theorem has been demonstrated both quantitatively and qualitatively. Figure 12 shows the adsorption (expressed in gram-molecules per square centimeter of surface for different bulk concentrations) for Dreft calculated from the surface tension-concentration curve. A similar curve is obtainable for sodium oleate, since dT/dC is the only variable.

According to the theory of frothing, a stable froth can be obtained only when dT/dC is numerically greater than zero, and either positive or negative. Accordingly, in Figure 11, there are three points corresponding to lack of frothing ability. These are points A, B, and C respectively. Unfortunately this was not realized until too late to make experimental determinations, and confirmation of this is not possible at this time.


Adsorption - Dreft
700 x 10 -15
600 x 10 -15
500 x 10 -15
400 x 10 -15
300 x 10 -15
200 x 10 -15
100 x 10 -15
0
90
80
70
60
50
40
30
20
10
0
Solute Concentration: 1 part solute per x parts solution
(Thousands)

Fig 12

MEASUREMENTS OF REFRACTIVE INDICES OF FROTHER SOLUTIONS

During the earlier part of this investigation the suggestion of Bartsch (quoted in the Introduction to this paper) to the effect that frother incompatibility might be due to a mutual lowering of solubility was constantly kept in mind. Solubilities of frothers such as pine oil and amyl alcohol are quite low, and it was difficult to visualize a satisfactory method of determining solubilities without using complicated chemical methods. Further, as the work proceeded, it was realized that the suggested explanation was not satisfactory for the phenomenon in the case of sodium oleate, which exhibits complicated solubility relationships. Thus, McBain (9) has shown that sodium palmitate (NaP, P = $C_{15}H_{31}COO^-$) dissociates " to give P^- anions which agglomerate to form highly hydrous colloidal particles that have the formula $(P^-)_n mH_2O$, in which n may be of the order 10-20. In other concentration ranges, neutral colloidal soap particles, $(NaP)_x mH_2O$, may exist, and at still others, there may be no colloidal particles but only: NaP = Na^+ and P^-. Thus, the nature of a soap solution varies with its concentration and also with its temperature. McBain and Bowden (10) point out that the ionic micelle must contain a certain amount of neutral colloid and therefore should be formulated $(NaP)_x(P^-)_n(H_2O)_m$; but the amount of NaP_x is small compared to $(P^-)_n$, most of the $(NaP)_x$ existing independently as neutral micelles."

However, after some preliminary work, it was ascertained that measurements of refractive indices of solutions of frothers were capable of yielding reasonably precise values of solubilities of some of these frothers and hence their concentrations in other than saturated solutions. Refractive indices were measured in a Zeiss dipping refractometer. (Figure 13)

Saturated solutions of n-amyl alcohol and terpineol were made up in a separatory funnel by thoroughly shaking excess solute with water and allowing the mixture to stand for a minimum period of twenty-four hours to insure segregation of the lighter frother from the underlying saturated solution. When ready for use, a definite amount of saturated solution was drawn from the funnel, placed in a constant temperature bath, and brought to room temperature. A small representative portion was taken for the determination and then returned to the original solution. Cumulative additions of water gave readings through the same range of concentration that was used in the previous surface tension measurements.

A similar procedure was adopted for sodium oleate , dreft, pine oil plus sodium oleate, and amyl alcohol plus sodium oleate.

To find the solubility of the solutes the indices of refraction were found for pure water and for the pure solution. These were plotted using percentage composition as the abscissa and the index of refraction as the ordinate. The method is best illustrated by referring to Figure 14. The

Figure 13

Zeiss Dipping Refractometer

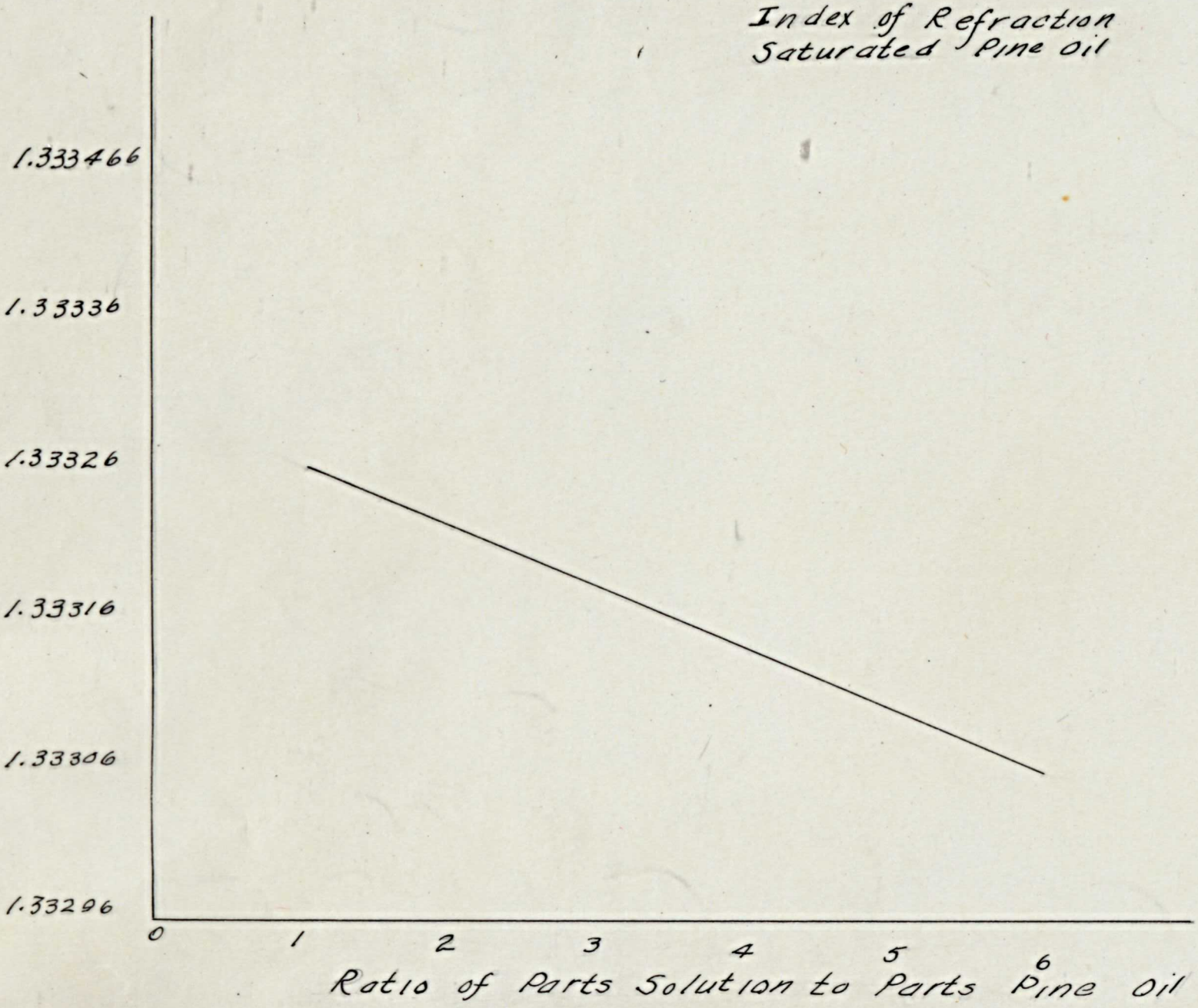

Index of Refraction
Saturated Pine Oil
1.333466
1.33336
1.33326
1.33316
1.33306
1.33296
0
1
2
3
4
5
6
Ratio of Parts Solution to Parts Pine Oil

Fig. 14

refractive index of pure water is 1.332966 at 20.5 degrees Centigrade. For pine oil the refractive index (obtained on an Abbe refractometer, (Figure 15) is 1.48105 at the same temperature. By connecting these two points together by a straight line, the relationship between any solution composition and its corresponding refractive index is given. The basic assumption, that refractive index is proportional to composition, is open to question, but the writer believes that the error involved, where only a small portion of the working curve is used, as in the case of these frothers of low solubility, is small and may be safely neglected in the present investigation.

Actually, in the case of pine oil, the measured refractive indices are proportional to the composition (Figure 14). Using this method, a solubility of 0.25 percent (by volume) is obtained for pine oil in water. For terpineol and amyl alcohol the relationship is not linear (Figure 16), but in the small concentrations used the error involved in assuming a linear relationship is small.

Refractive index-dilution curves for sodium oleate and for Dreft are unusual (Figure 17). The results are so unusual that duplicate tests were made, but with identical results. This is not the place to discuss the probable reasons for the curves obtained, and it will suffice to state that the complicated micellar structure of the colloids involved and subsequent ionization undoubtedly are reflected in the results.

Measurements of saturated pine oil-water solutions to which increments of sodium oleate solution were added showed no change in refractive index. Amyl alcohol solutions gave

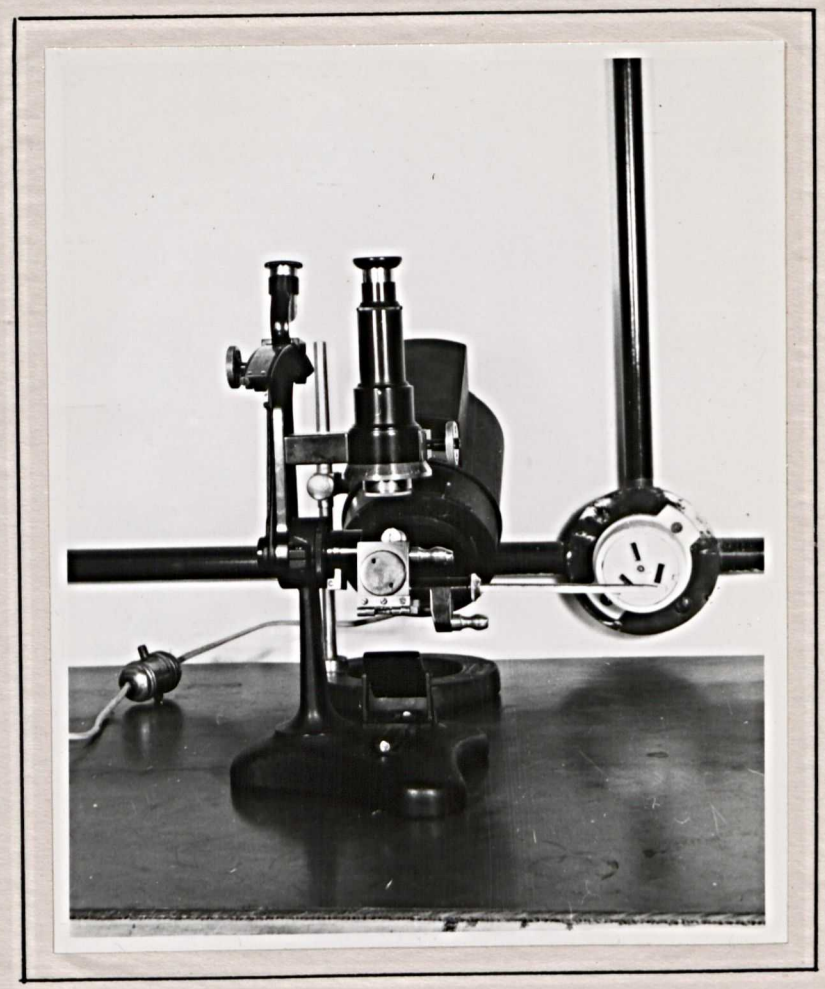


Figure 15

Abbe Refractometer

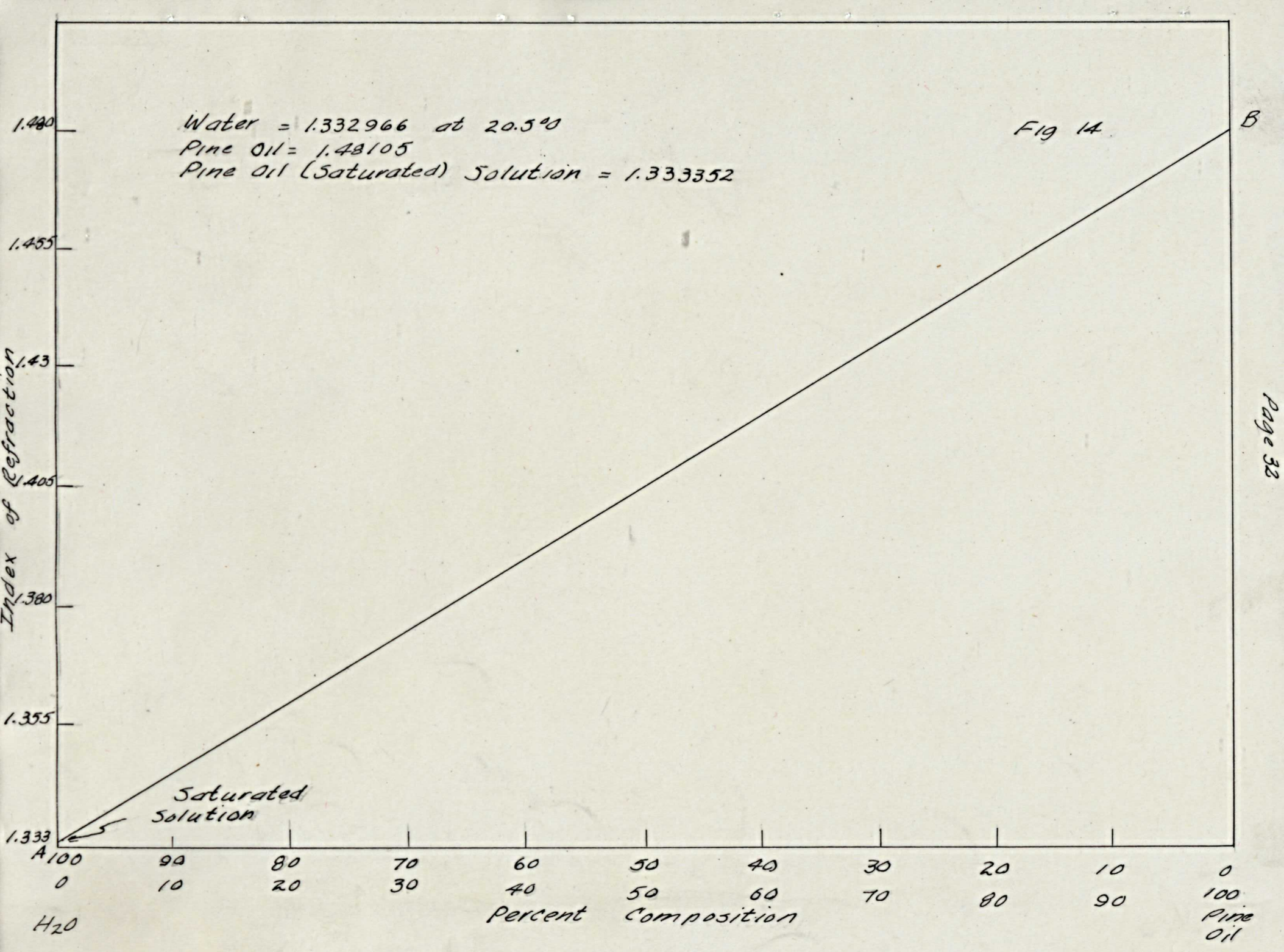
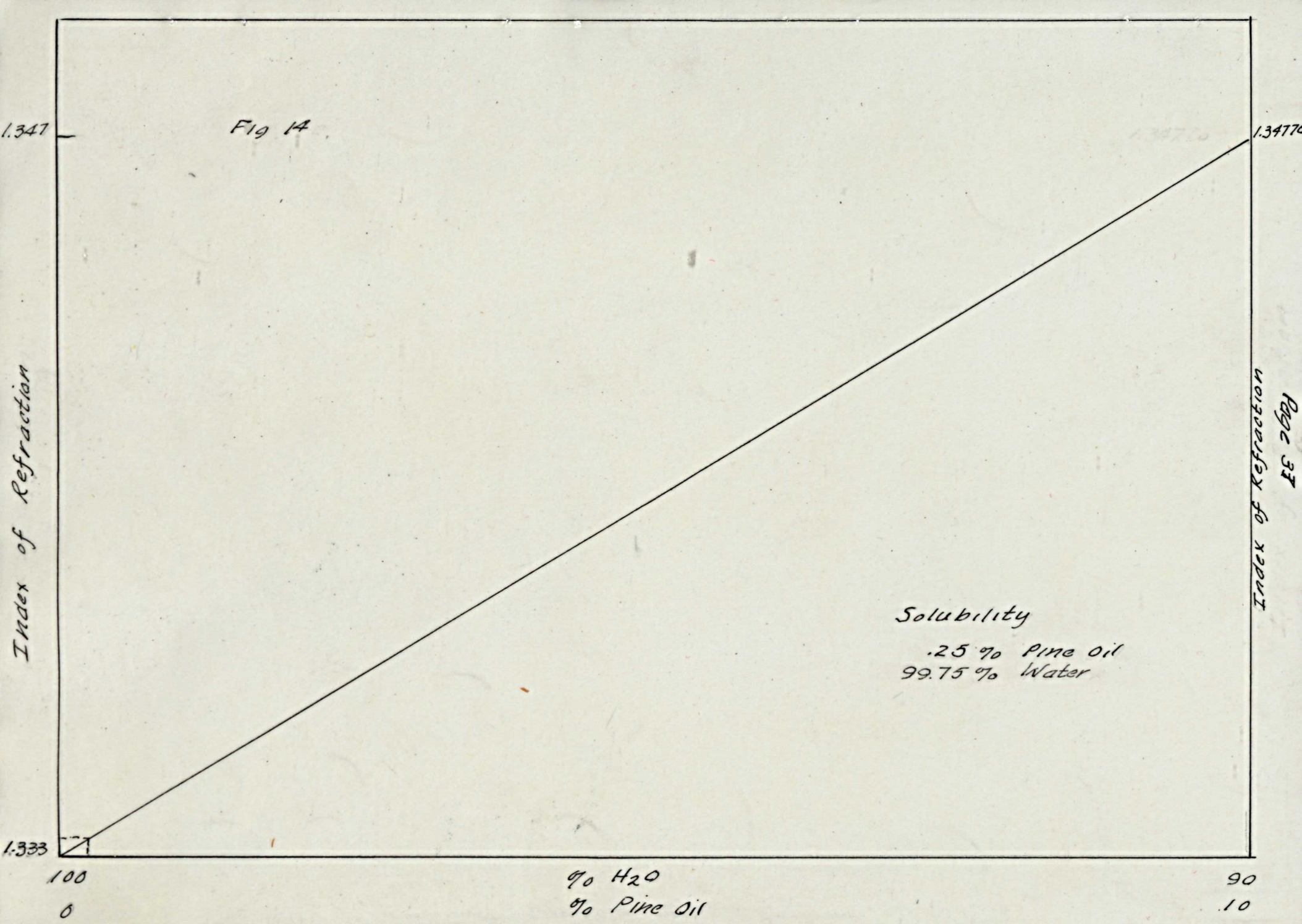

Water = 1.332966 at 20.5°
Pine Oil = 1.48105
Pine Oil (Saturated) Solution = 1.333352
Fig 14
B
A
Saturated Solution
Index of Refraction
1.480
1.455
1.43
1.405
1.380
1.355
1.333
100 90 80 70 60 50 40 30 20 10 0
0 10 20 30 40 50 60 70 80 90 100
H2O
Percent Composition
Pine Oil

Fig 14



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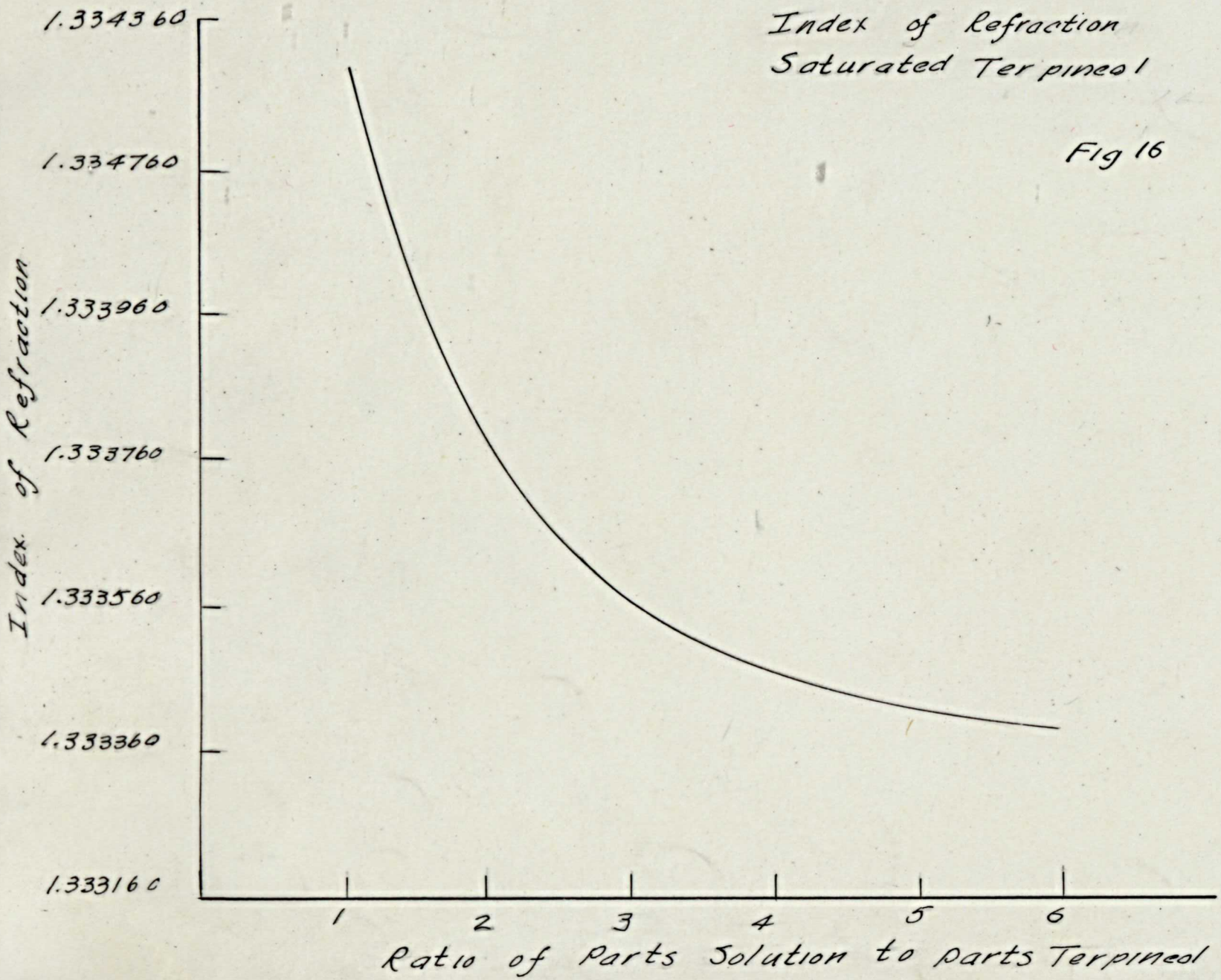
Index of Refraction
Saturated Terpineol

Fig 16



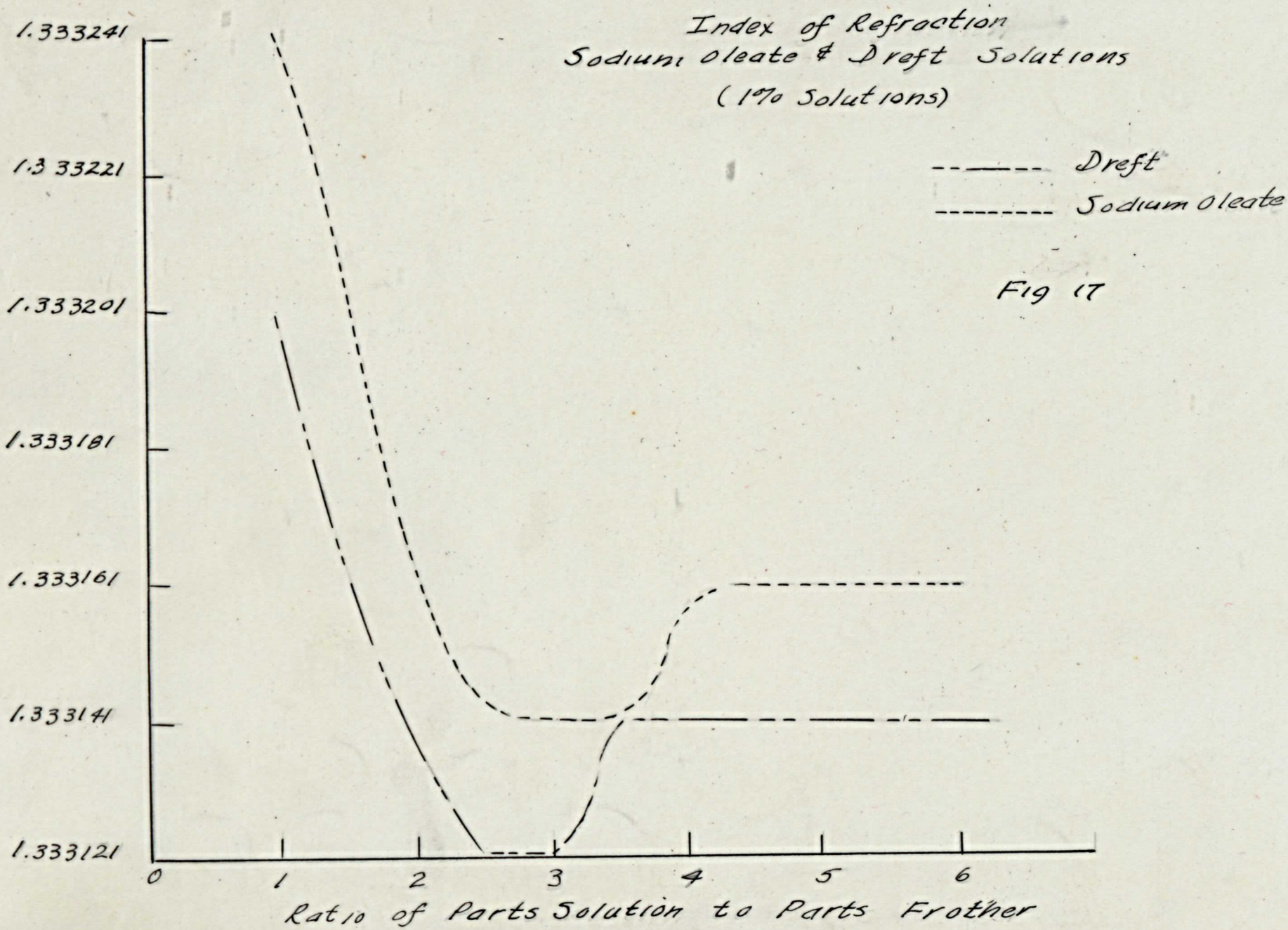

Index of Refraction
Sodium oleate & Dreft Solutions
(1% Solutions)
Dreft
Sodium Oleate
1.333241
1.333221
1.333201
1.333181
1.333161
1.333141
1.333121
0
1
2
3
4
5
6
Ratio of Parts Solution to Parts Frother

Fig 17

the same results. In other words, the solubility of the pine oil or of the amyl alcohol is not diminished by addition of a second frother (sodium oleate). This effectively disposes of the theory of lowered solubility offered by Bartsch, and requires formulation of a new theory to account for the phenomenon of frother incompatibility.

INCOMPATIBILITY AND EMULSIFICATION

Figure 8 shows how addition of excess oleate will cause destruction of a pine oil froth and formulation of an oleate froth. Once the oleate froth has been established, it may be destroyed and a pine oil froth reestablished by addition of sufficient pine oil. It would seem that simple emulsification of a weaker emulsifier by a stronger emulsifier furnishes an adequate explanation of frother incompatibility.

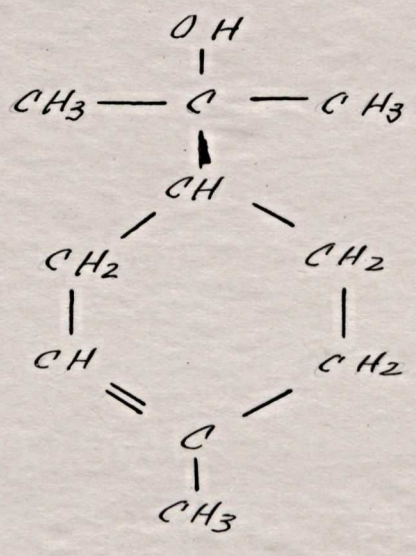
Thus, pine oil is a mild detergent. Sodium oleate is a strong detergent (11). The theory offered by the writer is that the stronger of two detergent reagents will destroy the frothing power of the weaker by a process of emulsification, removing the molecules from the air-water interface. After emulsification, and provided there is sufficient emulsifier remaining, the froth produced will be that due to the stronger emulsifier. Addition of more of the weaker detergent will abstract the stronger and give a reversal of the phenomenon provided a sufficient amount is used.

This sequence was tried in the previously described pneumatic frothing apparatus, with accordant results. Several mixtures were used, starting with ten drops of pine oil in 125 cubic centimeters of water, and ending with one drop of pine oil in the same quantity of water. To each, amyl alcohol was added, drop by drop. No minimum was observed in the pine oil-amyl alcohol-water system, which on the basis of the theory outlined above would indicate similar detergency for pine oil and amyl alcohol.

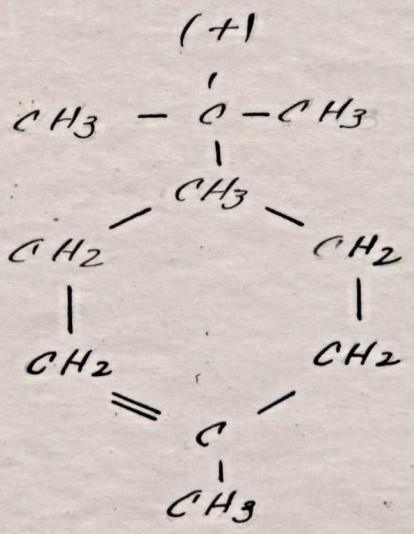
Pine oil-Emulsol-water and pine oil-sodium oleate-water systems gave no frothing at certain relative concentrations of the two frothers, with well marked frothing when one or the other frother was in excess.

CATAPHORESIS EXPERIMENTS

If we conceive of pine oil mechanically dispersed (or emulsified) in water, without addition of a third protective phase (such as an emulsifier) we would expect the droplets to acquire an overall positive charge. Pine oil is a mixture of terpene, pinene and terpineol. The first two are inactive as regards frothing (being hydrocarbons), but terpineol is an alcohol with one hydrophilic -OH group, as shown.



When this ionizes we have:



As the cation has lipophilic properties it should be adsorbed readily by the droplets of pine oil in the dispersion, and so give the droplets a positive charge.

Conversely, a suspension of sodium oleate in water should furnish lipophilic anions as shown:

$$CH_3(CH_2)_7 \cdot CH = CH \cdot (CH_2)_7 COONa \rightleftarrows [CH_3(CH_2)_7 CH = CH(CH_2)_7 COO]^- + Na^+$$

Assuming that the sodium oleate acts as an emulsifier (or emulsion stabilizing agent) for pine oil when oleate is added to a pine oil suspension because the oleate ions are adsorbed by the pine oil droplets, then the pine oil droplets should change from a net positive charge in water to a net negative charge.

To test this reasoning a Burton cataphoresis cell was set up (Figure 18). As pine oil dispersions and sodium oleate emulsions are essentially colorless, making it difficult to determine boundaries, a fat-soluble dye (such as is used in coloring margarine) was mixed with the reagents. This dye colored the pine oil droplets and the oleate particles so that the movement of of the boundary between suspension and distilled water could be observed under the influence of an electric potential.

The sodium oleate (1% solution) was definitely negatively charged as was pine oil emulsified in water with sodium oleate. The pine oil, mechanically dispersed in the water, gave apparently contradictory results. Droplets in the anode arm of the cell moved to the anode, those in the

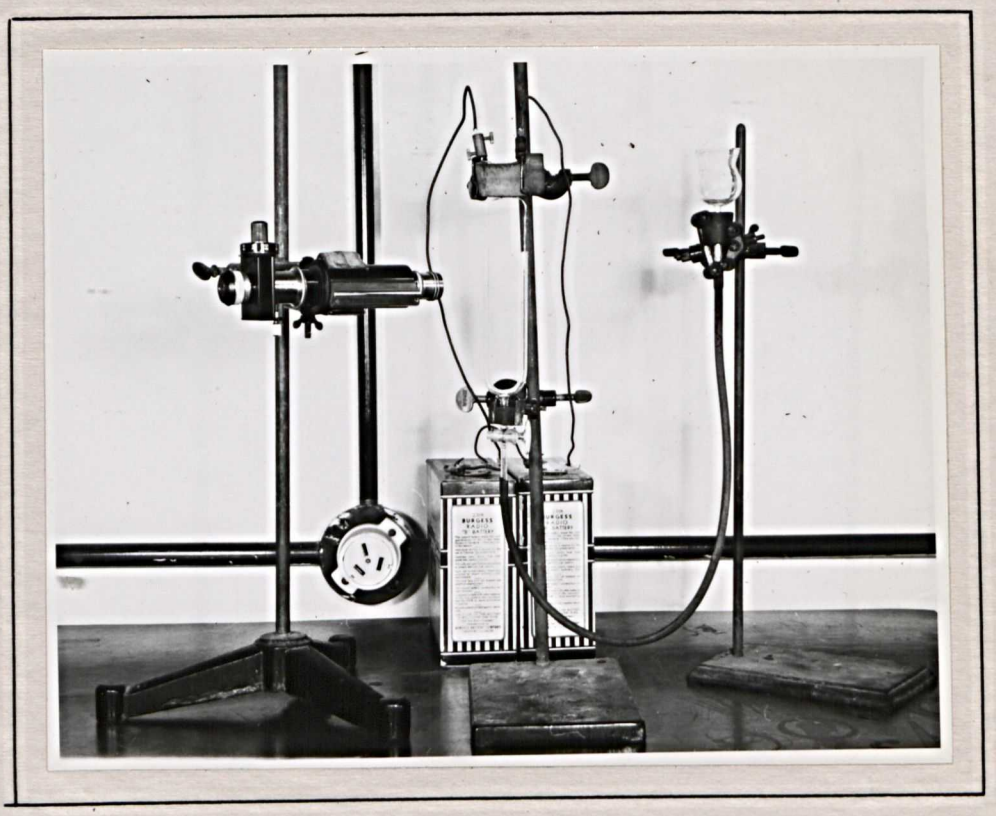


Figure 18

Cataphoresis Cell

cathode arm moved to the cathode. This was undoubtedly due to the coarse nature of the mechanical dispersion, the individual drops having sufficient buoyancy (Sp.Gr. pine oil 0,906) to cause them to move against the electric field and rise to the surface. In any event, there was no question of the negative charge on the particles in the pine oil-sodium oleate emulsion.

SUMMARY AND CONCLUSION

1. A pneumatic apparatus for measuring quantitatively the frothing ability of various frothing agents is described. This apparatus is capable of giving good results, particularly if the porous glass membrane is carefully made with the pores of the same size.
2. Use of a Fagergren laboratory flotation cell to quantitatively measure frothing ability is described. The results are reasonably concordant with, but not so easily obtained as, those given by the pneumatic apparatus.
3. The most marked instances of frother incompatibility were obtained with the pine oil-sodium oleate-water and the amyl alcohol-sodium oleate-water systems.
4. Surface tension measurements made on the pine oil-sodium oleate-water system with a DuNouy Tensiometer indicate that, at a definite pine oil concentration, various oleate concentrations have but little effect on the surface tension. The effect, though small, seems to be significant, and may indicate zero frothing for several oleate concentrations, the pine oil concentration being held constant. The results do not seem applicable to those obtained with the pneumatic apparatus.
5. Accurate measurements of refractive indices of solutions of frothers give information which may be used to (a) calculate the solubility of frothers in water and to (b) measure the amount of frother present in any solution of that

frother. The information obtained indicates that frother incompatibility is not due to mutual lowering of solubility. The refractive index method has other possible applications in flotation, such as the determination of the solubility of slightly soluble salts and collectors.

6. Although further confirmatory work is necessary, the theory that incompatibility of sodium oleate and pine oil as frothers is due to emulsification of the pine oil by the more strongly detergent oleate seems to be fairly well established, and it is definitely proven that it is not due to lowering of solubility as advocated by Bartsch.

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